

Quantum Efficiency Determination by Fluorescence in an Integrating Sphere: Consistency of a Simple, Transparent Solution with a More Complex, Widely Used Solution

by Larry D. Merkle

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Quantum Efficiency Determination by Fluorescence in an Integrating Sphere: Consistency of a Simple, Transparent Solution with a More Complex, Widely Used Solution

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14. ABSTRACT <p>Quantum efficiency (QE) is an important factor in determining the overall efficiency of a solid-state laser, but can be very difficult to measure. One approach to obtain an absolute value for the QE of a laser material involves fluorescence and scattering measurements in an integrating sphere. A successful method for such measurements was developed by de Mello et al. and has been applied by a number of groups. Yet its base equations leave open questions as to the accuracy of some terms, and the form of their solution for QE is not easy to interpret. Since this leaves open the possibility that their approach is not as accurate as might be hoped, we have undertaken an analysis that accounts for the photons at each stage of the measurement, using the same underlying assumptions about the physical processes as de Mello et al. We find a much simpler solution whose interpretation is quite transparent and show that it is fully consistent with their solution.</p>					
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1. Introduction

Solid-state lasers operating at high power levels can be very useful, not only for military applications, but also in manufacturing and medicine. Keeping power requirements realistic, minimizing thermal management, and optimizing beam quality all require that the laser be as efficient as possible. One of the several factors that need to be quantified and optimized is the laser material's fluorescence quantum efficiency (QE). For an optically pumped laser, this is defined as the ratio of the number of photons emitted as fluorescence to the number absorbed from the pump source. Excitations that do not lead to optical emission generally release their energy as heat, not only reducing laser efficiency but also directly contributing to the heat load. Thus, a high QE is doubly important.

There are several ways in which QE might be measured, each with its limitations. Broadly, the main techniques involve the temperature dependence of the excited state's total decay rate, the direct measurement of the heat generated, and the direct measurement of the light emitted. In the latter two cases, one must also choose between relative measurements, in which the material under study is compared to a standard with known QE, and absolute measurements that do not rely on such a comparison.

The temperature-dependent decay rate technique relies on the fact that many causes of reduced QE affect every laser ion in the material, but do not shorten the decay rate so much as to make the fluorescence undetectable. Further, many such mechanisms depend on the population of phonons available, making the decay rate strongly dependent on temperature. However, some mechanisms for low QE de-excite some laser ions so severely that they do not fluoresce at all. As a result, they cannot be detected by this technique, so that the true QE may be lower than that observed, sometimes by a large margin.

Direct detection of the thermal energy generated upon excitation of the laser ions avoids this problem, since the excitation energy released by non-fluorescing laser ions contributes to the heat being detected. One generally detects the thermal energy by measuring the temperature increase of the sample upon excitation at a known rate. Detection may be by thermocouple, piezoelectric transducer, thermal camera, or the measurement of optical distortions due to the sample's thermal expansion and the temperature dependence of its refractive index. However, each of these methods requires knowledge of appropriate thermal properties, such as the specific heat, thermal diffusivity, and/or thermal expansion coefficient, among others. Further, specific techniques have their own unique pitfalls, such as the need to make excellent thermal contact with the sample when using a thermocouple or piezoelectric transducer.

The detection of the light emitted by the sample avoids many of those difficulties, but introduces its own set of challenges. In principle, the amount of energy emitted as light is compared to the

energy absorbed to excite the sample, the ratio giving the QE after correction for the photon energies involved. Correction must also be made for the wavelength dependence of the detection system's sensitivity. In practice, however, almost all fluorescence detection methods yield a signal only proportional to the energy emitted rather than absolute values, with the proportionality constant being extremely difficult to determine with any accuracy. One response to this difficulty is to make relative measurements, comparing the fluorescence signal from the sample under study with that from a material whose QE is known. However, differences between the samples in sample geometry, absorption of excitation light, or reabsorption of the fluorescence can undermine the accuracy of such relative measurements.

“Absolute” measurements of the optical power emitted as fluorescence upon the absorption of a known excitation (or pump) power can be made, eliminating some of the problems noted above, but at the cost of introducing some unique challenges. In this context, “absolute” means that comparison of the sample under study with a known material is not required. A promising way to do this is with an integrating sphere. An integrating sphere surrounds the sample as completely as practicable with a shell of material that is highly reflective and scatters light over all directions, thereby homogenizing any light generated within that enclosure or introduced to it from outside (1, 2). A detector attached to a port in the sphere thus gives a signal very representative of the light emitted by the sample. It also gives a signal representative of the pump light introduced from the outside, so that comparison may be made between fluorescence and excitation. This homogenization effectively removes the problems of sample geometry (and resulting direction-dependence of fluorescence intensity) and polarization of the fluorescence or the pump beam. If the sphere and detector are properly calibrated, the relative strengths of the fluorescence and pump signals accurately reflect the relative strengths of actual photon fluxes of each, thereby enabling calculation of QE.

Several years ago, de Mello et al. (3) presented a useful approach to determining QE from integrating sphere measurements. Their technique is best suited to the case in which the sample has negligible probability of reabsorbing the fluorescence, and in such cases, it is being used by a number of groups, examples of which can be found in references 4–6. The experiments required are straightforward, as are the equations proposed for the analysis. Yet, there are some aspects of those equations that are not obvious, and the resulting formula for QE includes factors whose meaning and necessity are not clear.

This report describes an analysis of the steps involved in the detection of pump light and fluorescence in an integrating sphere. Although it uses the same physical assumptions as those made by de Mello et al., our way of following photons through the system leads to different equations to be solved and results in different solutions. We show that these solutions are fully consistent with that of de Mello et al., but their meaning is more transparent.

2. The Approach of de Mello et al.

The strategy of de Mello et al. (3) for determining QE is based on a set of three experiments, as sketched in figure 1. The black circle indicates the integrating sphere, with ports for introducing the pump light (typically a laser beam, here indicated in blue), a sample holder (the thick vertical line), and the multimode optical fiber (shown in brown) that takes scattered and fluorescence light to a spectrometer. There is a baffle (the horizontal line) in front of the optical fiber port to assure that light reaching the fiber must scatter off the sphere at least once.

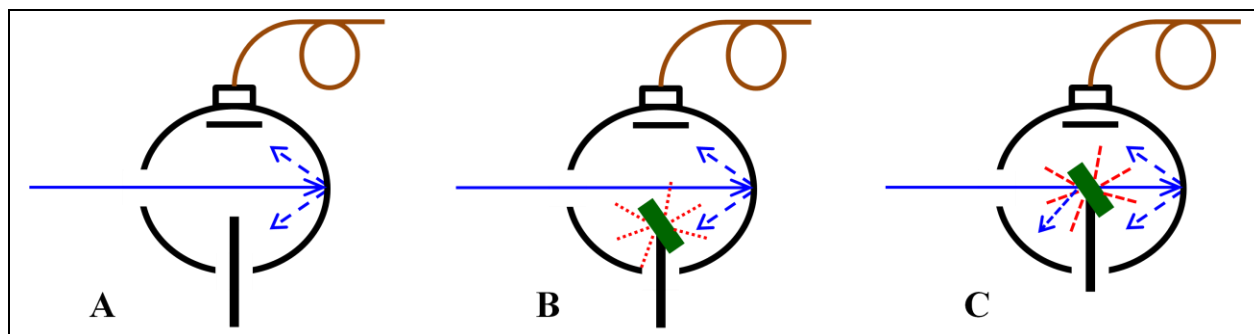


Figure 1. The three experiments used by de Mello et al to determine QE. A: “Empty” sphere (no sample); B: sample in sphere but outside the pump beam; C: sample in the pump beam. The solid blue line is the pump laser beam, dashed blue lines indicate scattered laser light, red dashed or dotted lines indicate fluorescence from the sample, which is the green rectangle. The brown curve is the multimode optical fiber that delivers light from the sphere to an optical spectrometer (not shown,) the horizontal black line is a light baffle and the vertical black line is the sample holder.

In experiment A, there is no sample in the integrating sphere—only the empty sample holder. Thus, the detection system sees only the scattered laser beam, giving a signal L_e (where “e” denotes “empty” sphere.) In experiment B, the sample has been introduced into the sphere, but is outside the laser beam. It can fluoresce when excited by scattered laser light, but this fluorescence is typically weak. The detection system sees light from two sources (distinguished by the spectrometer on the basis of their spectra): scattered laser L_o and fluorescence F_o . In experiment C, the sample has been translated into the laser beam. Care is taken to tilt the sample so that reflections of the laser beam do not exit any of the sphere’s ports. The detection system now sees scattered laser L_i and fluorescence F_i . In each experiment, the scattered laser and fluorescence signals are corrected for the wavelength response of the sphere and detection system, and are converted to be proportional to the relevant photon flux, rather than to power density. Due to the system response correction, the constant of proportionality can be taken as the same for all five quantities.

Their determination of the QE from these experiments is based on the following definitions and equations. The QE is η , the fraction of scattered laser light absorbed by the sample is μ , and the

fraction of incident laser light absorbed by the sample in experiment C is denoted A. As a result, the physical relationships among the various beams can be expressed in the following equations.

$$L_o = L_e \times (1 - \mu) \quad (1)$$

$$L_i = L_e \times (1 - A) \times (1 - \mu) \quad (2)$$

$$L_o + F_o = L_o + (\mu L_o \eta) \quad (3)$$

$$L_i + F_i = (1 - A)L_o + AL_e\eta + (1 - A)F_o \quad (4)$$

Equations 1 and 2 follow straightforwardly from the definitions of μ and A. The second term in equation 3 indicates that the fluorescence photon flux must be the pump laser's photon flux times the fraction of that flux absorbed by the sample times the fraction of that absorbed flux emitted as fluorescence. In equation 4, the first term (for the scattered laser signal in experiment C) again follows from the definition of A, as does the third term (for the fluorescence due to scattered laser light,) and the second term is the analogous expression for fluorescence due to light absorbed directly from the incident beam.

From these equations, simple algebra enables one to obtain the various parameters in terms of the measured quantities.

$$A = 1 - L_i/L_o \quad (5)$$

$$\mu = 1 - L_o/L_e \quad (6)$$

$$\eta = \frac{F_i - \frac{L_i}{L_o}F_o}{(1 - \frac{L_i}{L_o})L_e} \quad (7)$$

Equation 7 is the desired result—the QE in terms of measured quantities, assuming negligible reabsorption of the fluorescence by the sample.

This method, including the result in equation 7, was tested a few years ago by a group from Durham University and Horiba Jobin Yvon Ltd. (4). They performed the requisite experiments and calculations on several materials whose QEs have been determined by other means and reported in the literature, achieving satisfactory agreement in each case.

Despite this success, questions can be raised regarding the results of de Mello et al. The scattered laser light involves multiple reflections of light in the sphere, with some light reaching the detector after only one reflection, some after two reflections, and so on. The same is true for the fluorescence signal. How is this handled in equations 1–4? The term in equation 4 that denotes the fluorescence due to direct excitation of the sample by the incident beam is expressed in terms of L_e , yet that expression is as much the result of multiple reflections as any of laser and fluorescence signals. Is that consistent? Also, why does the QE result, equation 7, contain factors of L_i/L_o whose meaning in that context is not immediately obvious? From the point of view of simple photon accounting, one might expect the QE to be given by the photon flux emitted when

the sample is in the beam, divided by the pump photon flux absorbed, which, in turn, would be given by the difference between the laser signal for the empty sphere and that observed when the sample is in the beam. Indeed, some groups have used an expression just that simple (7, 8).

3. Analysis of the Experiments Taking Multiple Reflections into Account

Due to the questions noted above, we think it worthwhile to reexamine the process from a different perspective. We analyze the same set of three experiments, but treat explicitly the multiple reflections (that is, scattering) off the surface of the sphere (and sample holder) that affect what light signature reaches the detection system, and we make explicit the correction of data for the system's spectral response. To make that treatment simple enough for clarity, we treat the correction at only two wavelengths—the pump laser wavelength and an effective fluorescence wavelength that may represent a weighted average over the entire fluorescence spectrum. We also treat each pass of light reflected by the sphere as following the same equations describing the average behavior, so as to avoid complications such as some light rays missing the sample after a given reflection off the sphere wall, others going through the sample face-on, still other edge-on, etc.

This approach, treating as it does the average interaction of the light on each pass through the sphere rather than the overall results, requires a somewhat different set of parameters than does the approach of de Mello et al. A and η have the same definitions as before, but now f is the fraction of scattered laser light absorbed by the sample on any one pass. This is therefore the product of the fraction of scattered light that encounters the sample and the fraction of such incident light that is absorbed. (This fraction absorbed is not necessarily the same as A , since the scattered light encounters the sample from a distribution of all possible directions.) L_{inc} is the incident laser photon flux, B_L is the detection efficiency of the system at the laser wavelength and B_F is that at the effective fluorescence wavelength. Similarly, r_L and r_F are the effective reflectivities of the integrating sphere at the same two wavelengths. These effective reflectivities include not only the actual reflectivity of the sphere material, but also the losses due to the fact that on each pass across the sphere, some fraction of the scattered light encounters the ports in the sphere and exits.

Since all the spectra must be corrected for the wavelength response of the system, we treat the effect of multiple reflections in the sphere on that correction. Some signal can reach the optical fiber and thereby the detection system after only one reflection off the sphere's scattering material, other light after two such reflections, and so on. This makes the total signal an infinite series. If we denote the system response at a given wavelength as $R(\lambda)$, then the response of the combined sphere and detection system is as follows.

$$R(\lambda) = B(\lambda) \times [r(\lambda) + r(\lambda)^2 + \dots + r(\lambda)^n + \dots] = B(\lambda) \times \frac{r(\lambda)}{1-r(\lambda)} \quad (8)$$

Thus, for the laser and effective fluorescence wavelengths, we can express the system response as $R_L = B_L \times r_L / (1 - r_L)$ and $R_f = B_f \times r_f / (1 - r_f)$. To correct each measured quantity for system response, the raw measurement is divided by the applicable R.

Accounting for the multiple reflections of scattered laser light in each of the three experiments in the same way as was done for the spectral response measurement and recalling that the incident laser flux is L_{inc} , we have the following expressions. For the empty sphere,

$$L_e = B_L \times \frac{L_{inc}}{R_L} \times [r_L + r_L^2 + \dots + r_L^n + \dots] = B_L \times L_{inc} \times \frac{1 - r_L}{B_L r_L} \times \frac{r_L}{1 - r_L} \quad (9a)$$

and thus

$$L_e = L_{inc}. \quad (9b)$$

For the sample in the sphere but out of the beam,

$$\begin{aligned} L_o &= B_L \times \frac{L_{inc}}{R_L} \times [r_L + r_L^2 \times (1 - f) + \dots + r_L^n (1 - f)^{n-1} + \dots] \\ &= B_L \times L_{inc} \times \frac{1 - r_L}{B_L r_L} \times \frac{r_L}{1 - r_L (1 - f)} \end{aligned} \quad (10a)$$

and thus

$$L_o = L_{inc} \times \frac{1 - r_L}{1 - r_L (1 - f)}. \quad (10b)$$

For the sample in the laser beam,

$$L_i = (1 - A) \times \frac{B_L L_{inc}}{R_L} \times [r_L + r_L^2 \times (1 - f) + \dots + r_L^n (1 - f)^{n-1} + \dots] \quad (11a)$$

and thus

$$L_i = L_{inc} \times (1 - A) \times \frac{1 - r_L}{1 - r_L (1 - f)}. \quad (11b)$$

Additional care is needed when considering the fluorescence signals, as two infinite sums are involved. One is due to the fact that the sample may be excited by scattered laser light after one, two, or more reflections off the sphere wall. The other is due to the fact that, after fluorescence occurs, fluorescence photons may reach the detection system after one, two, or more reflections. Thus, the total fluorescence signal reaching the detection system is that which would apply if the light went straight to the optical fiber times a factor S, given as follows:

$$S = r_f + r_f^2 + \dots + r_f^n + \dots = \frac{r_f}{1 - r_f}. \quad (12)$$

The fluorescence signal for the sample out of the beam is as follows.

$$F_o = B_f \times \frac{L_{inc}}{R_f} \times [r_L f \eta S + r_L^2 (1 - f) f \eta S + \dots + r_L^n (1 - f)^{n-1} f \eta S + \dots] \quad (13a)$$

and thus

$$F_o = L_{inc} \times f \times \eta \times \frac{r_L}{1 - r_L(1-f)}. \quad (13b)$$

The fluorescence signal for the sample in the laser beam is the sum of a term similar to the above and a term due to fluorescence excited directly by the incident beam.

$$\begin{aligned} F_i &= B_f \times \frac{L_{inc}}{R_f} \\ &\times \{A\eta S + (1 - A) \times [r_L f \eta S + r_L^2 (1 - f) f \eta S + \dots + r_L^n (1 - f)^{n-1} f \eta S + \dots]\} \\ &= L_{inc} \times \eta \times \left\{ A + (1 - A) \times \frac{r_L f}{1 - r_L(1-f)} \right\} \end{aligned} \quad (14a)$$

and thus

$$F_i = L_{inc} \times \eta \times \frac{A - A r_L + r_L f}{1 - r_L(1-f)}. \quad (14b)$$

Given these equations, rearrangement to express the QE in terms of measured quantities proceeds as follows. Division of equation 11b by equation 10b gives

$$A = 1 - \frac{L_i}{L_o} \quad (15)$$

just as in equation 5, the solution of de Mello et al. Division of equation 10b by equation 9b gives

$$f = \frac{1 - r_L}{r_L} \times \left(\frac{L_e}{L_o} - 1 \right) \quad (16)$$

which leaves r_L undetermined, but will prove to be sufficient. Substitution of equations 15 and 16 into equation 14b and division by equation 9b gives the following.

$$\frac{F_i}{L_e} = \eta \times (1 - r_L) \times \frac{1 - \frac{L_i}{L_o} + \frac{L_e}{L_o} - 1}{(1 - r_L) \times \frac{L_e}{L_o}}. \quad (17)$$

This simplifies to one form of the desired result:

$$\eta = \frac{F_i}{L_e - L_i}. \quad (18)$$

Substitution into equation 13b gives a similar result:

$$\eta = \frac{F_o}{L_e - L_o}. \quad (19)$$

Note that both of these solutions, equations 18 and 19, are considerably simpler than that of de Mello et al. Each requires only two measurements, rather than three. (Referring to figure 1, these are experiments A and C for equation 18, and experiments A and B for equation 19.) Further, each conforms to the expectations of simple photon accounting, namely, that for a given experiment with the sample in the sphere, the QE should be given by number of photons emitted divided by the number of pump photons absorbed.

4. Relationship Between the Present Solutions and That of de Mello et al.

Because the solution of de Mello et al. is less transparently related to a simple counting up of all photons in the experiment, some algebra is required to check whether the two sets of solutions are equivalent. This is most straightforwardly done by rearranging the de Mello et al. solution as follows:

$$\eta = \frac{F_i - \frac{L_i}{L_o} \times F_o}{\left(1 - \frac{L_i}{L_o}\right) \times L_e} = \frac{L_o \times F_i}{L_e \times (L_o - L_i)} - \frac{L_i \times F_o}{L_e \times (L_o - L_i)}. \quad (20)$$

Multiply and divide by factors that permit isolation of recognizable patterns:

$$\eta = \frac{L_o \times (L_e - L_i)}{L_e \times (L_o - L_i)} \times \frac{F_i}{L_e - L_i} - \frac{L_i \times (L_e - L_o)}{L_e \times (L_o - L_i)} \times \frac{F_o}{L_e - L_o}. \quad (21)$$

According to our solutions, equations 18 and 19, the second fraction in each term should equal η . Making those substitutions gives the following result:

$$\eta = \frac{L_o \times (L_e - L_i)}{L_e \times (L_o - L_i)} \times \eta - \frac{L_i \times (L_e - L_o)}{L_e \times (L_o - L_i)} \times \eta. \quad (22)$$

It is trivial to show that, if the three η 's are indeed equal, the left- and right-hand sides of equation 22 are equal. Thus, these solutions for η are mutually consistent.

5. Relative Sensitivity to Uncertainty in the Measured Quantities

Given that our solutions and that of de Mello et al. are equivalent, is there any advantage in choosing one over another? One consideration is sensitivity to errors in the measured quantities. These may be due to noise, drift in the baseline, and error in the system calibration curves (due, for example, to differences in path length through humid air between the calibration and fluorescence experiments), among others. Table 1 presents the laser and fluorescence fluences calculated for a few combinations of the parameters in the model of section 3, and the resulting QEs calculated using the two solutions presented in that section and the solution of de Mello et al. Because F_o , the fluorescence signal with the sample outside the beam, is smaller than F_i , it is more affected by types of measurement error that are of similar magnitude for both signals. As a result, the QE solution in terms of F_o and L_o (equation 19) tends to be very sensitive to measurement errors and is the least attractive of the three solutions. Of course, as the lines labeled Case B and Case D show, sources of error that are proportional to the signal strength give the same sensitivity to errors for both equations 18 and 19. There is little difference in sensitivity to errors between the de Mello et al. solution (equation 7) and our solution in terms of F_i and L_i solution (equation 18). This is the case because, when F_o is much smaller than F_i , the de Mello et

al. solution is dominated by F_i , and thus resembles equation 18 more closely. Since their solution (equation 7) involves the difference between F_i and a term involving F_o , it becomes somewhat more sensitive to error when F_o becomes more similar to F_i in magnitude. Thus, on the whole, this work's solution in terms of F_i and L_i , equation 17, tends to be the least sensitive to noise and other sources of measurement error.

Table 1. Sensitivity of different QE solutions to variations in F_i and F_o . The laser and fluorescence fluences L_e , L_o , L_i , F_o , and F_i are defined in the text. η is the quantum efficiency. Case A: all fluences consistent with a single set of model parameters (A , r_L and f); Case B: F_o too large by 1%; Case C: F_o too large by $0.01 \times F_i$; and Case D: F_i too large by 1%.

Case	L_e	L_o	L_i	F_o	F_i	η (this work) equation 17	η (this work) equation 18	η (de Mello) equation 7
A	1.0000	0.9991	0.4996	0.00081	0.4504	0.9000	0.9000	0.9000
B				0.00082	0.4504	0.9000	0.9090	0.9000
C				0.00531	0.4504	0.9000	5.9090	0.8955
D				0.00081	0.4549	0.9090	0.9000	0.9090
A	1.0000	0.9991	0.4996	0.00045	0.2502	0.5000	0.5000	0.5000
B				0.00045	0.2502	0.5000	0.5050	0.5000
C				0.00295	0.2502	0.5000	3.2828	0.4975
D				0.00045	0.2527	0.5050	0.5000	0.5050
A	1.0000	0.9091	0.4545	0.04545	0.2727	0.5000	0.5000	0.5000
B				0.04591	0.2727	0.5000	0.5050	0.4995
C				0.04818	0.2727	0.5000	0.5300	0.4973
D				0.04545	0.2755	0.5050	0.5000	0.5055
A	1.0000	0.6667	0.3333	0.30000	0.6000	0.9000	0.9000	0.9000
B				0.30300	0.6000	0.9000	0.9090	0.8970
C				0.30600	0.6000	0.9000	0.9180	0.8940
D				0.30000	0.6060	0.9090	0.9000	0.9120

6. Summary and Conclusions

In this work, the determination of QE from the set of experiments proposed by de Mello et al. (3) has been analyzed from a different perspective than theirs. Our analysis follows the infinite series of reflections of the spectral calibration source, the pump laser, and the fluorescence within the integrating sphere. Thus, it gives improved confidence that the main details of the process have been taken into account, at least for the case in which reabsorption of fluorescence by the sample can be neglected. Our solutions are simpler and are more readily seen to be consistent with intuitive photon accounting approaches (7, 8).

Analysis shows that our solutions and theirs are consistent, so that the choice of which to use can be made on grounds other than validity. Numerical tests indicate that our solution based on spectra with the sample in the pump beam is somewhat more robust against errors in the measured quantities, though the difference is not large.

A substantial practical advantage of either one of our solutions is that it requires only two measurements rather than three. In particular, the more robust of the two (equation 18) requires only the spectrum of the empty sphere (including the empty sample holder, since its reflectance may not be identical to that of the sphere) and the spectrum with the sample in the pump beam. The combination of simplicity of the experiments and solution, transparent interpretation, somewhat reduced sensitivity to measurement error, and proven consistency with the de Mello et al. result makes the solution embodied in equation 18 an attractive way to evaluate QE based on integrating sphere experiments.

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